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Conversion of Ammonia Plants to Methanol Production

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Technical Report

Conversion of Ammonia Plants to Methanol Production

by

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February 1982

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16. ABSTRACT

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Summary

This report investigated the technical feasibility and capital cost of converting an ammonia plant to a methanol plant, both using natural gas as a feedstock. It was determined that the ammonia industry, which currently produces about 20 million tons of ammonia per year in the U.S., could convert their facilities to produce 16.4 million tons per year of methanol, or a fuel oil equivalent of 150,000 barrels per day. Such a conversion would cost about $2.1 billion, compared to a cost of $3.1 billion for building new natural gas-based methanol plants of the same capacity. While converting ammonia plants to methanol production has favorable capital costs over that of building new plants, the savings of one-third is not large, particularly considering the effects of eliminating (or reducing) ammonia production. Thus, it would appear at this time that large savings cannot be obtained from the conversion of ammonia plants to methanol production.

Conversion of Ammonia Plants to Methanol Production

The U.S. ammonia industry currently produces over 20 million tons of ammonia,[1] primarily for use in the fertilizer industry. Ammonia is also used as the starting point of most military explosives, and it touches some aspect of nearly all other industries in the U.S.[2] Methanol is also an important product of the U.S. chemical industry, and with a growing interest in methanol as a transportation fuel, an increase in its production may become even more desirable in the future. Although ammonia and methanol appear to be chemically dissimilar, both compounds can be commercially synthesized from the same feedstock, which is primarily natural gas. With future demand of methanol possibly escalating, an investigation may be necessary to evaluate the feasibility and the cost of converting an existing natural gas based ammonia plant to the production of methanol.

Although ammonia appears to be substantially different in chemical composition from methanol, much of the commercial synthesis process is very similar for the two chemical compounds. Both can be synthesized from the same feedstock which is primarily natural gas, to produce the large amounts of hydrogen needed. The major difference between these two commercial syntheses is that in ammonia production, all carbon containing gases (particularly carbon monoxide and carbon dioxide) are removed so that only nitrogen and hydrogen remain to react, while in methanol synthesis, a considerable amount of carbon monoxide is retained along with the hydrogen and no nitrogen is allowed to enter the system.

This report will analyze and discuss the feasibility and the cost of converting an ammonia plant to production of methanol. The first section of this report will outline the major steps involved with the established industrial production of ammonia.

In the section following this, the conversion of an ammonia plant to a methanol plant will be examined. This report will then determine the total potential U.S. capacity of methanol production from converted ammonia plants, and the cost of this conversion on a plant basis and a nationwide basis.

I. Description of the Commercial Production of Ammonia[2,3]

The overall commercial synthesis of ammonia involves the reaction of nitrogen from air and hydrogen from natural gas at a ratio of 1:3 at high pressure and relatively low temperature in the presence of a catalyst. This overall chemical reaction is:

$$1/2\ N_2(g) + 3/2\ H_2(g) = NH_3(g)$$

A typical flow diagram for the commercial production of ammonia is shown in Figure 1. As was mentioned above, natural gas is at present the most common feedstock used for production of ammonia. The basic steps shown in Figure 1 for converting natural gas into ammonia will be discussed in this section. These steps are desulfurization, primary and secondary reforming, shift conversion, carbon dioxide removal, synthesis gas purification, and ammonia synthesis and recovery.

In the first step, natural gas (which is essentially methane) is introduced and desulfurized. Much of the feed natural gas, or methane, is contaminated with sulfur-containing compounds which may poison catalysts downstream in the ammonia synthesis process. Desulfurization involves the absorption of sulfur-containing compounds (which is usually in the form of hydrogen disulfide) onto activated carbon or zinc oxide. After desulfurization, the purified natural gas is ready for reacting in the next steps of steam reforming.

As shown in Figure 1, the steam reforming steps of the purified natural gas feedstock is carried out in two catalytic reaction stages. The first stage is called the primary reformer, where the methane is mixed with superheated steam and reacted over a catalyst to produce a partially reformed gas, consisting of carbon monoxide, hydrogen and unreacted methane. The overall reaction of the primary reformer is:

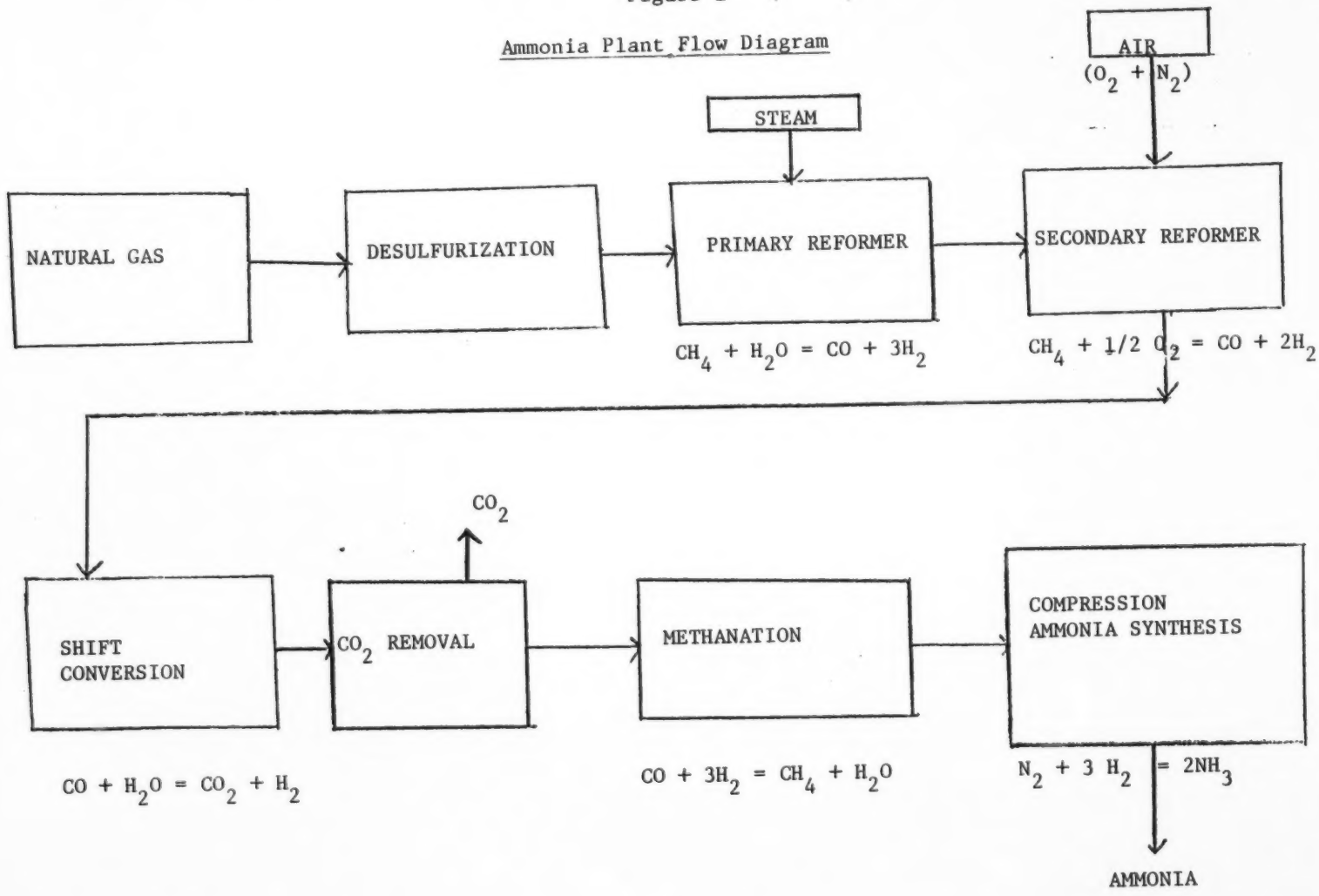
$$CH_4 + H_2O = CO + 3\ H_2 \text{ (Primary reforming)}$$

Primary reforming is carried out in a furnace to accomodate the large heat transfer required. The exit gas temperature is about 750°-850°C and pressure is about 415-515 psig. The type of catalyst used depends on the temperature and pressure in the primary reformer.

The next step is the secondary reformer where the reforming reaction is carried out to completion (all of the methane reacted)

Figure 1

Ammonia Plant Flow Diagram



also with a catalyst. As shown in Figure 1, sufficient air is added to the secondary reformer, serving a dual purpose. First, the combustion of methane and oxygen provides heat, which is used to react the remaining methane and steam to form more carbon monoxide and hydrogen. Second, nitrogen (via the air) is also added to the system in the amount required later in the ammonia synthesis process. This amount of air is adjusted to eventually supply a hydrogen/nitrogen ratio of 3:1. A nickel catalyst supported on alumina is generally used in the secondary reformer. Thus, while the primary reformer is used for reforming methane only, the secondary reformer is used for both completing the reforming process and providing the necessary nitrogen required later in ammonia synthesis. The overall reaction involved in the secondary reformer is:

$$CH_4 + 1/2\ O_2 + 2N_2 = CO + 2H_2 + 2N_2$$

After the primary and secondary reformers, the next step of CO shift conversion is applied as shown in Figure 1. CO shift conversion utilizes the water-gas shift reaction and produces hydrogen from carbon monoxide via the following reaction:

$$CO + H_2O = CO_2 + H_2 \text{ (Shift reaction)}$$

The bulk of the carbon monoxide is first shifted to carbon dioxide in a high temperature shift converter (HTS) operating at 350°-450°C. The gases are then cooled and most of the remaining carbon monoxide from the HTS is shifted to carbon dioxide in a lower temperature shift converter (LTS) at a temperature of about 200°-250°C. The HTS catalyst consists mainly of iron oxide and chromium oxide. The LTS catalyst consists of copper oxide supported on zinc oxide and alumina.

The effluent gases leaving the LTS converter from the shift conversion step thus contain carbon dioxide which must be removed or it will poison catalysts used in later steps. Most of the carbon dioxide is removed in the bulk removal step (as shown in Figure 1), where it is reduced to trace amounts. In removing the carbon dioxide, scrubbing with an gaseous solution of monoethanolamine (MEA) or a hot solution of potassium carbonate is standard. Activated carbon may also be used as a means to remove carbon dioxide.

After bulk carbon dioxide removal, methanation is applied, where any residual carbon monoxide and carbon dioxide are converted to methane, since any carbon, oxygen, or oxygen-containing compounds poison the ammonia synthesizing catalyst in the last step of the ammonia synthesis process. Methanation, which is essentially the reverse of the reforming reactions, involves the following two reactions:

$$CO + 3H_2 = CH_4 + H_2O$$

$$CO_2 + 4H_2 = CH_4 + 2\ H_2O$$

Temperatures are typically in the range of 300-400°C and the catalyst is usually nickel supported on alumina, kaolin, or calcium aluminate cement.

After this step, the carbon monoxide and carbon dioxide content of the treated gas is only a few parts per million and does not affect the remainder of the ammonia synthesis process. However, the methane itself contains carbon and must be eliminated. A cryogenic purifier system (which is not shown in Figure 1 as a distinct unit) is then used to remove all of the water and nearly all the methane. In this unit the gas from methanation is first dried to a very low dew point, then cooled and expanded in a turbine to liquefy a portion of the gas. After further cooling, the vapor from the partially liquified stream is scrubbed in a rectifying column to remove the required amount of the methane.

The synthesis gas is now ready for the final step of compression and ammonia manufacture in the synthesis loop. This is shown as the compression ammonia synthesis unit in Figure 1. The reaction is:

$$N_2 + 3H_2 = 2NH_3$$

The operating pressures for most synthesis loops fall in the range of 150-200 atm (2200-2940 psig). This final step involves a catalyst which generally consists of iron with the addition of oxides of aluminum and potassium. Unreacted gases are recycled. In almost all plants ammonia is recovered by condensation. This requires refrigeration, normally provided by the synthesis ammonia itself. Inerts entering the system are normally removed with a purge stream.

II. Conversion of an Ammonia Plant to Methanol Production[2,3]

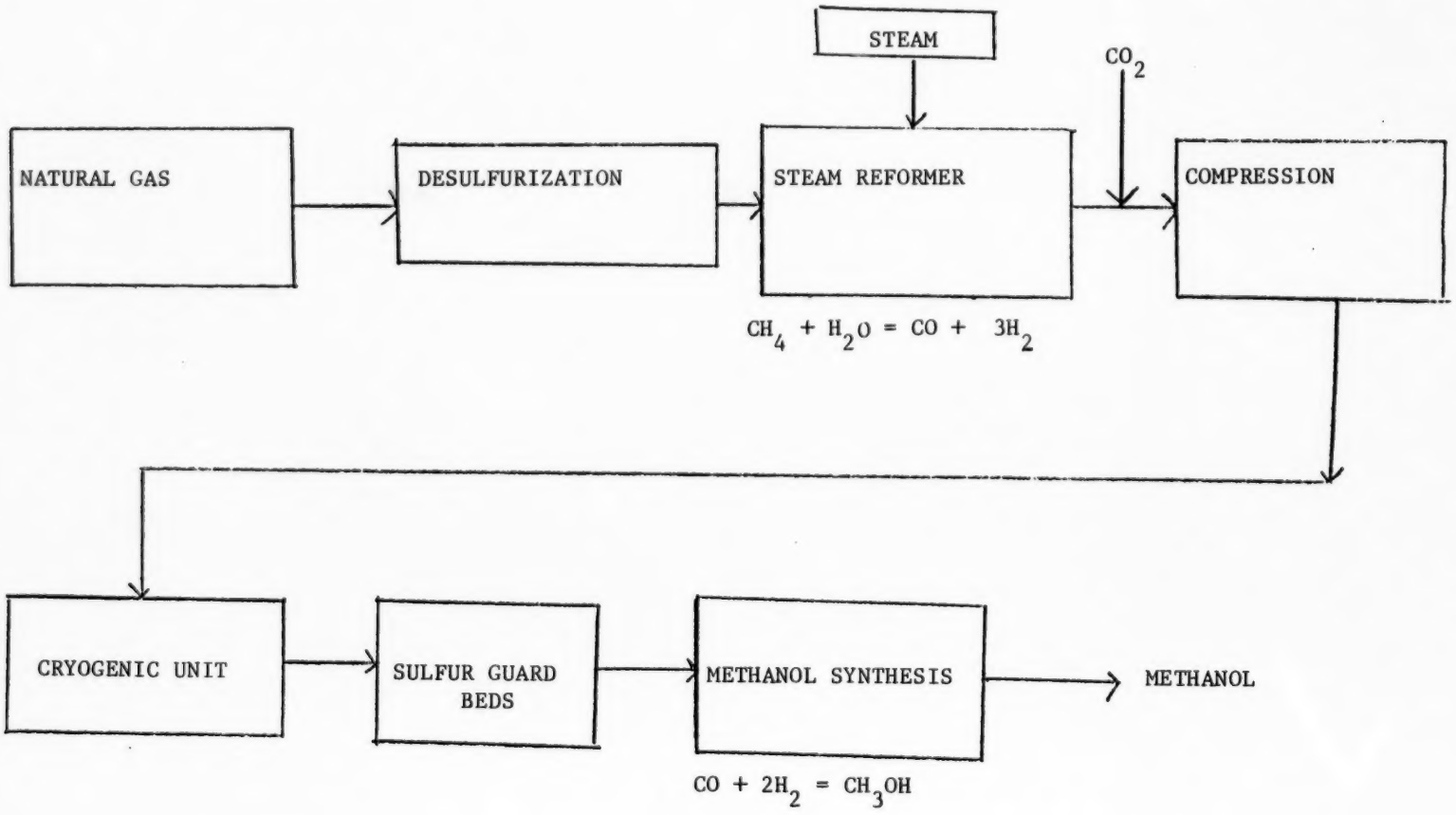
Commercial synthesis of methanol involves the reaction of carbon monoxide and hydrogen, both which can be obtained from a natural gas feedstock, at an overall ratio of 1:2. High temperatures and pressures are used, in addition to a catalyst to speed up the reaction. The overall reaction is:

$$CO + 2H_2 = CH_3OH$$

A flow diagram representing a typical commercial methanol production process is shown in Figure 2. When comparing Figure 2 to the ammonia plant flow diagram of Figure 1, it can be seen that the initial steps of both processes are similar. However, methanol production also involves additional steps which replace many of the steps involved with ammonia production. The basic steps shown in Figure 2 for production of methanol from a converted ammonia plant are desulfurization, steam reforming, compression,

Figure 2

Methanol Flow Diagram From Converted Ammonia Plant



cryogenic purification, final sulfur removal, and methanol synthesis. These steps will be discussed below.

The first step of methanol production is the desulfurization of natural gas, which was also the first step of ammonia production. As with ammonia production the natural gas used for methanol production must be processed free of sulfur to prevent poisoning catalysts downsteam. After desulfurization the next step is steam reforming again similar to ammonia production. For methanol production, only one reformer is typically used which also involves the introduction of steam, as shown in Figure 2. In the reformer unit, the steam and methane react to form carbon monoxide and hydrogen, identical to the reaction occurring in the primary reformer for ammonia production. This reaction is expressed as:

$$CH_4 + H_2O = CO + 3H_2$$

The steam reformer in methanol production produces a carbon monoxide:hydrogen ratio of 1:3, while methanol synthesis requires only a 1:2 ratio. Thus, as shown in Figure 2, carbon dioxide is added to produce carbon monoxide and consume hydrogen via the reverse of the water gas shift reaction discussed above.

The steps following the steam reformer in methanol synthesis differ from that found in ammonia synthesis. First of all, the secondary reformer the carbon monoxide shift converters and the carbon monoxide removal unit are unnecessary for methanol production. Also, the process of methanation in an ammonia plant is also eliminated in methanol production, because it is desired to retain as much carbon monoxide as possible.

However, there are additional steps in the production of methanol which are not present in the production of ammonia. The first step is the compression of carbon monoxide and hydrogen that has exited from the reformer. This step improves the conversion of these reactants in the methanol synthesis unit. A turbo-driv centrigual compressor is usually used to compress the carbon monoxide:hydrogen mixture from about 150 atm to 300 atm. Following the compression step, nearly all of the carbon dioxide and steam left are removed in a standard cryogenic feed purification unit. A new cryogenic unit must be installed since a higher pressure is used for methanol synthesis than is used for ammonia synthesis. A second cryogenic unit is also necessary to separate the dry, carbon dioxide-free gas into synthesis gas (H_2/CO ratio = 2, CH_4 + N_2 about 1 percent) and a tail gas which is used as fuel gas and consists mainly of unreacted methane with some carbon monoxide. The cryogenic units are shown together in Figure 2.

Following the two cryogenic units, the synthesis gas is heated and passed through a zinc-oxide sulfur-guard bed for final removal of hydrogen sulfide and other sulfur-containing com-

pounds. After this comes the methanol synthesis where a new reactor (again because of higher pressures than ammonia synthesis) is required. The final reaction taking place in the reactor is:

$$2H_2 + CO = CH_3OH$$

The methanol is subsequently cooled and condensed. Most of the synthesis gas passing through this unit is not converted to methanol and is recycled and mixed with fresh, incoming synthesis gas.

In summary, the following units must be added to an ammonia plant to convert it to methanol production: the compression unit, two cryogenic units, the sulfur guard bed units, and the methanol synthesis unit.

III. Capacity for Methanol Production

The above section described the steps involved with conversion of an ammonia plant to methanol production. This section will estimate the nationwide capacity of methanol production from converted ammonia plants.

The nationwide capacity of methanol production from a converted ammonia plant depends upon two factors. First, the ratio of methanol to ammonia produced must be determined, based on an equal amount of natural gas feed. Second, the current nationwide production capacity of ammonia must be determined. These two factors will be examined below.

The ratio of methanol to ammonia production can be based on a stoichiometric estimate which assumes the same amount of natural gas feedstock in both cases. For ammonia synthesis, the limiting factor is the production of hydrogen which results in the production of about 4.86 tons of ammonia for every ton of methane feed. For methanol synthesis, the limiting factor is the production of carbon monoxide which results in the production of about 4 tons of methanol for every ton of methane feed. Thus, on this basis the ratio (by weight) of methanol to ammonia production capacity is 0.82.

Now, the total ammonia production capacity for the U.S. must be estimated. Current (1981) U.S. ammonia production capacity should be close to 20 million tons based on an estimate by a recent report on the ammonia industry.[4] In that report, 1981 ammonia production estimates are broken down by each ammonia producing company and location, and are based on actual February 1979 production data. There are 81 plants in operation in the U.S. producing these 20 million tons annually.[4] The producers of this ammonia and the locations of their plants are shown in Table 1.[4]

Table 1

1981 Ammonia Production Capacity*

Company	Location	1,000 Tons Per Year
Agrico Chemical Co.	Blytheville, AR	407
	Donaldsonville, LA	468
	Verdigris, OK	840
Air Products & Chemical Co.	New Orleans, LA	210
	Pace Junction, FL	100
Allied Chemical Corp.	La Platte, NE	172
	Hopewell, VA	340
	Helena, AR	210
American Cyanamid Co.	Fortier, LA	340
	Fortier, LA	240
Amoco Oil Co.	Texas City, TX	522
Apache Powder Co.	Benson, AZ	15
Atlas Chemical Co.	Joplin, MO	136
Beker Industries	Conda, ID	100
Borden Chemical Co.	Geismar, LA	340
Camex, Inc.	Borger, TX	400
Car-ren	Columbus, MS	
CF Industries, Inc.	Donaldsonville, LA	375
	Donaldsonville, LA	375
	Donaldsonville, LA	420
	Donaldsonville, LA	420
	Fremont, NE	48
	Terre Haute, IN	150
Chevron Chemical Co.	Pascagoula, MS	510
	Fort Madison, IA	105
	El Segundo, CA	20
Columbia Nitrogen	Augusta, GA	510
Diamond Shamrock	Dumax, TX	160
Dow Chemical	Freeport, TX	115
E. I. DuPont de Nemours	Beaumont, TX	340
	Victoria, TX	100

Table 1 (Cont'd)

1981 Ammonia Production Capacity

Company	Location	1000 Tons Per Year
El Paso Products	Odessa, TX	115
Farmland Industries	Fort Dodge, IA	210
	Dodge City, KS	210
	Hastings, NE	140
	Enid, OK	840
	Lawrence, KS	340
	Pollock, LA	420
Farmers Chem-CF Ind.	Tyner, TN	170
Felmont Oil Corp.	Olean, NY	85
First Miss Corp.	Fort Madison, IA	365
FMC Corp.	S. Charleston, WV	24
Gardinier, Inc.	Tampa, FL	120
Georgia Pacific	Plaquemine, LA	196
Grace-Okla. Nitrogen	Woodward, OK	400
W. R. Grace & Co.	Woodstock, TN	340
Green Valley Chemical	Creston, IA	35
Hawkeye Chemical	Clinton, IA	138
Hercules, Inc.	Louisiana, MO	70
Hooker Chemical Co.	Tacoma, WA	23
International Minerals & Chemicals	Sterington, LA	400
Jupiter Chemical (Terra)	Lake Charles, LA	78
Kaiser Agricultural Chemicals	Savawnnah, GA	150
Mississippi Chemical	Yazoo City, MS	393
Corp.	Pascagoula, MS	175
Monsanto Co.	Luling, LA	850
NJ Zinc-Gulf and Western	Palmerton, PA	35

Table 1 (Cont'd)

1981 Ammonia Production Capacity

Company	Location	1000 Tons Per Year
N-Ren Corp. (Cherokee N)	Pryor, OK	94
N-Ren Corp. (St. Paul Ammonia)	East Dubuque, IL	238
Occidental Chemical Co.	Taft, LA	90
	Lathrop, CA	160
	Plainview, TX	52
Olin Corporation	Lake Charles, LA	490
Pennwalt Chemical Corp.	Portland, OR	8
Philips Pacific Chemicals	Beatrice, NE	210
PPG Industries	Natrium, WV	50
Reichhold Chemicals	St. Helens, OR	90
J. R. Simplot	Pocatello, ID	108
Tennessee Valley Authority	Muscle Shoals, AL	74
Terra Chemicals	Port Neal, LA	210
Triad Chemical	Donaldsonville, LA	340
Union Oil Co.	Kenai, AK	1,020
	Brea, CA	280
U.S.A. Petrochem Corp.	Ventura, CA	60
USS Agri-Chemicals	Clairton, PA	325
	Cherokee, AL	177
	Geneva, UT	70
Valley Nitrogen Producers	El Centro, CA	210
Vistron Corp.	Lima, OH	475
Vulcan Materials	Witchita, KS	35
Wycon Chemical Co.	Cheyenne, WY	167
Total		20,000

* Based on future projections from February, 1979 data as estimated in ref. [4].

Next, using the ratio of methanol to ammonia production determined above, the nationwide production capacity of methanol from converted ammonia plants can be estimated for 1981. The nationwide production for methanol is about 16.4 million tons per year. The specific volume of methanol is about 7.2 barrels per ton, so the annual volumetric production capacity would be 118 million barrels. On a calender day operating basis, the daily production would be about 320,000 barrels. On an energy basis, this is equivalent to a production of 150,000 barrels of fuel oil equivalent per day (BFOE/D)(based on an energy value of 2.11 barrels of methanol per barrel of fuel oil equivalent).

IV. Cost

The total capital cost of this conversion will be estimated in this section. To determine these costs, capital costs will be determined first for each converted ammonia plant. The cost of each plant depends upon the plant size. The 81 U.S. ammonia plants vary from a production of 8,000 tons per year (or 22 tons per day) to a production as large as one million tons per year (or 2,790 tons per day).[4] Rather than attempt to calculate the cost plant by plant, a cost for an average plant size will be estimated for convenience. A straight average of the 81 ammonia plants, based on a nationwide production of 20 million tons per year, would yield a plant size of about 250,000 tons per year, or about 700 tons of ammonia per day. If these were converted to methanol, each methanol plant would have the capacity to produce about 550 tons of methanol per day. On an energy equivalent basis, this would amount to 1,990 BFOE/D.

Now that the average size plant has been determined, the cost of converting an average-sized ammonia plant to a methanol plant must be estimated. In section II above, it was determined that the addition of the following units would be necessary when converting an ammonia plant to methanol production: a compression unit, two cryogenic units, sulfur guard beds, and a methanol synthesis unit. The cost for these additional units for converting to this average size methanol production plant is shown in Table 2. These costs were scaled to a production of 550 TPD from plant sizes found in current studies,[5,6,7,8,9] ranging from a production of 1800 TPD to 75,000 TPD methanol using a scaling factor of 0.75. This is a common capital scaling factor for chemical producing industries.[10] Table 2 shows the middle of the range of these scaled costs. The sum of these costs is $22 million (1981 dollars) per plant. In addition, there are probably other costs involved when converting from ammonia to methanol production. Since these costs would be difficult to estimate, a contingency factor of 20 percent will be allotted. Thus, the capital cost for the conversion units with contingency is $26 million for a 550 TPD plant. Since there are approximately 81 of these plants nationwide, the total cost to the nation would be approximately $2.1 billion.

Table 2

Cost of Methanol Producing Units
(Millions of First Quarter 1981 Dollars, 550 TPD)

Technology/Synthesis	Cost*
Synthesis Gas Compression	$ 1
Two Cryogenic Recovery Units	$ 4
Sulfur Removal and Recovery/Methanol Drying	$ 3
Methanol Synthesis	$14
Total	$22

* Costs are the middle of the range of costs found in current literature,[4,5,6,7,8] and are scaled to a methanol production of 550 TPD (1900 BFOE/D), using a 0.75 capital scaling factor.

The cost of converting an ammonia plant should be compared to the cost of constructing a new natural gas based methanol plant to observe the possible savings involved. According to a report by ICF,[11] the cost of a new methanol plant using natural gas as feedstock would be about $140 million (in 1981 dollars) for a 2,000 TPD plant. To accomplish an annual production of 16.4 million tons per year (or the amount if all ammonia plants were converted to methanol production), approximately 22 of these new methanol plants would be required. The total cost of these plants would be about $3.1 billion. This is approximately 50 percent higher than the nationwide cost of $2.1 billion determined above for converting the nation's ammonia plants to methanol production.

Thus, the cost of producing methanol from converted ammonia plants is about $2.1 billion nationwide and appears to be roughly one-third less expensive than building new methanol plants, which cost about $3.1 billion. Of course, in the long run, final justification of converting an ammonia plant to methanol production as opposed to building new plants would not be based on the simplified estimate of determining capital costs in each case. Instead, an investigation is necessary to weigh the economics of eliminating ammonia production and increasing methanol production. Such an economic study, however, is beyond the scope of this report. This report only shows that the capital costs for producing a determined amount of methanol are reduced by approximately one-third if ammonia plants are converted rather than if new methanol plants were constructed.

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